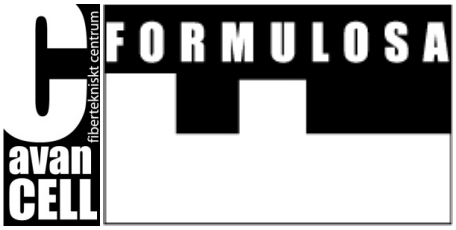
Masters Degree in Chemical Engineering

Freely Mouldable Cellulose

Synthesis, properties and further functionalization of Cellulose Acetoacetates

Master Thesis



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Resumo

Os produtos químicos são muito importantes em diferentes tipos de aplicações, um exemplo é a produção de alimentos, especialmente na protecção das embalagens que permitem a conservação de alimentos. O novo material de embalagem com recursos renováveis de base biológica tem como objectivo desenvolver um material moldável livremente. O material usado será baseado em celulose funcional em que o principal constituinte será de ésteres de celulose pois mostram grandes aplicações em plástico.

O projecto é baseado na síntese de Celulose Acetoacetatos, CAA, com dois reagentes diferentes, Diketene Analoge e um Ethylketene Dimer. A síntese pressupõe a obtenção de diferentes graus de substituição, alto e baixo. O grau de substituição é determinado por espectroscopia de Infravermelho e por Análise Elementar para as reacções homogéneas e heterogéneas. Por fim formar compósitos de fibras entre Celulose Acetoacetatos/ Polietileno e caracterizar os materiais com diferentes técnicas.

Na realização deste projecto foi possível obter diferentes valores de grau de substituição e materiais solúveis em Acetona. O grau de substituição foi obtido por Analise Elementar e a com a espectroscopia de Infravermelho foi possível concluir que se consegue modificar a Celulose com dois reagentes diferentes excepto na reacção heterogénea de baixo grau de substituição com Ethylketene Dimer.

Abstract

Chemicals are very important in many kind of applications. One example is with the food production and especially the protection of the packaging that enable the food conservation. New packaging materials from renewable bio-based resources, has the aim to develop a freely moldable material. The material will be based on chemical functionalized pulp. The main constituent of the pulp studied in this project is Cellulose Esters. Mainly Organic Esters Cellulose has shown plastic applications.

The project is based to synthesize Cellulose Acetoacetates with two different reagents, a Diketene Analoge and an Ethylketene Dimer. The synthesis should give Cellulose with different kind of degree of substitution (*DS*), high and low. The degree of substitution is determined by Infrared spectroscopy and Elemental Analysis for homogeneous and heterogeneous reactions. Finally compounding composites between Cellulose Acetoacetates/Polyethylene and characterize the material with different techniques.

In this work it was possible to obtain different values of degree of substitution and the material has different solubility in Acetone. The *DS* was determined by Elemental Analysis. From Infrared spectroscopy it was concluded that modified Cellulose was obtained from the two different reagents except in the heterogeneous reaction for low degree of substitution with Ethylketene Dimer.

Contents

Notation and Glossary

ΔP	Pressure	Bar
M	Torque	Ncm
μ	Viscosity	Pa.s
m	Weight	g
n	Number of moles	mmol
V	Volume	ml

List of Abbreviations

CAA	Cellulose Acetoacetates
MCC	Microcrystalline Cellulose
DMAC	N,N–Dimethylacetamide
LiCl	Lithium Chloride
DMF	N,N-Dimethylformamide
Et_3N	Triethylamine
NMP	1-Methyl-2-Pyrrolidinone
N_2	Nitrogen
IR	Infrared spectroscopy
DS	Degree of Substitution
EA	Elemental Analysis
NMR	Nuclear magnetic resonance
SA	Soluble in Acetone
NSA	Not Soluble in Acetone
DMA	Dynamic Mechanical Analysis
PE	Polyethylene

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1 Introduction

The material that surrounds us in these days is chemical-based. We can say that we make part of a chemical and physical system that forms the environmental and the society. The Chemistry has the objective to produce and transform basic materials into more complex products and materials that can help us in many different ways. Normally these substances are derived from natural resources, like crude oil, gas, sugars etc, that after refining give us a wide resource of materials that can be further functionalized.

The Chemicals are very important in much kind of applications like power-generating, storage systems, security, medical treatment, hygiene, modern textiles. Another application wherein Chemistry is important is food production and especially the protection by the packaging that enable the food conservation [1].

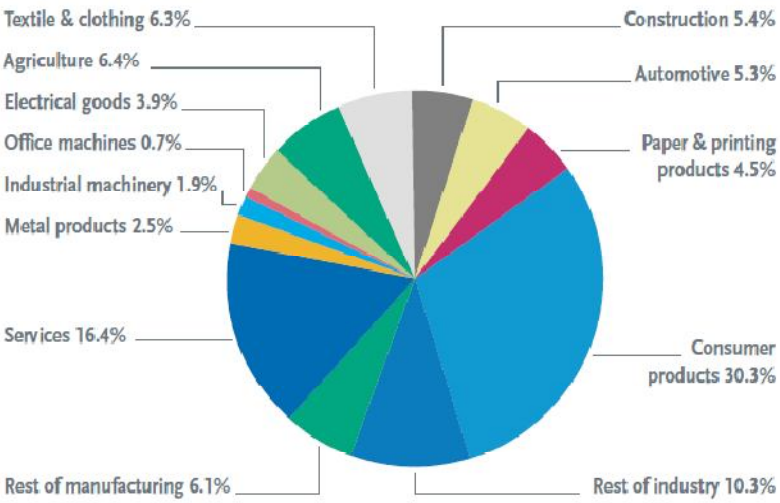


Figure 1: *The share of chemical domestic consumption [1].*

The most important areas of research with these chemicals are the Industrial Biotechnology, Material Technologies, Reaction and Process Design and Horizontal Issues, giving us proposals or solutions that allow the development of environment and society.

The Material Technology area focuses on materials for future surroundings, wherein of the most important sectors is the Nanotechnology. Nanotechnology is an important tool for understanding and for the development of new materials technologies [2].

Reaction and Process Design is applicable to all areas of chemistry and biotechnology because it integrates development via catalyst operation to product handling and logistics. This section enables us to know what method will be used in the development of appropriate products.

Finally the area that concerns Horizontal Issue is important in relation with necessary political, social and structural reforms to increase the society. The Horizontal arena is stimulating support for innovation and addressing societal concerns associated with new products and processes [2].

In the ***Table 1*** is represented some of the areas for development and their technology platforms.

Table 1: *Represent different platforms technologies in different areas of development [3].*

Technology Platforms	Material Technologies	Reaction and Process Design	Industrial Biotechnology
ACARE - Aeronautics	Light material, energy saving		
Photovoltaic	Materials with enhanced photon	Synthesis and purification of material	
Food for Life	New packaging materials, increased bioavailability of nutritional supplements	Formulation engineering, Encapsulation	Use of organic waste as feedstock
FTP - Forest Resources	Hybrid materials	Separation and purification technologies	Lignocellulose based biorefineries
ERTRAC – Road Transport	Energy storage systems	Collaborative/ inventory planning	Biofuels

We can see that some of the platforms have more than one area of research. In the case of this project the relevant technology platforms is Food for life and the Materials Technology. This project, new packaging materials from renewable bio-based resources, has the aim to develop a freely moldable material. The material will be based on chemical functionalized pulp. The pulp consists of three main constituents, cellulose, hemicelluloses and lignin. Cellulose and hemicelluloses are polysaccharides and cellulose consists of a linear chain of several hundred to over ten thousand β (1→4) linked D-glucose units whereas hemicelluloses consist of different types of saccharides [4].

The polysaccharide chains are organized into fibrils and are considered to form amorphous and crystalline parts.

Cellulose, the relevant polysaccharide for this project is a homopolymer, that has (1→4)-β-D-linked polyglucose units [4]. In ***Figure 2*** we can see the linear conformation of the Cellulose.

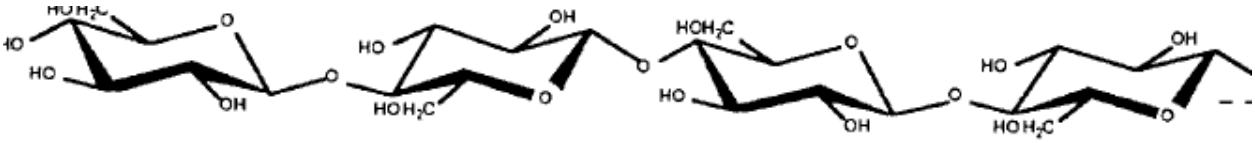


Figure 2: *Wobble helical zigzag conformation of Cellulose in pulp fiber [4].*

The cellulose can be functionalized in many different ways and two of the most effective ways to modify cellulose is by ester or ether functionalization

- **Cellulose Esters**, with a difference between;
    I. Inorganic Cellulose esters, who is for non-plastic application;
    II. Organic Cellulose esters, who can be used in plastic application;
- **Cellulose Ethers**, who can be used in plastic application;
- **Regenerated Cellulose**, with plastic application;

In this project the focus will be on the part of Organic Cellulose Esters and the aim is to find Cellulose esters, *Cellulose Acetoacetates* that can be freely shaped. Thus the project consists of three important parts of development and they are:

1) Synthesis of Acetoacetylated celluloses, CAA, with high and low degree of substitution. Both commercial available reagents as well as synthesized reagents will be prepared.
2) The Degree of substitution of the CAA will be determined from Elemental analysis and Infrared spectroscopy.
3) Synthesis of Acetoacetylated fibers, C_fAA and characterization of the material.

2 State of Art

Cellulose Esters offers a wide range of solubility and compatibility. One of the main suppliers is Eastman that sells a wide range of different Cellulose Ester. It produces a flexible film requiring little or no plasticizer in many applications. The types of Cellulose exhibit enviable film properties such as low color and good opposition to weathering.

The development of Synthesis of Acetoacetylated Cellulose and the Synthesis of Acetoacetylated fibers was very significant over the time. This developments show us how the experiment was made with different reagents and different techniques.

2.1 Synthesis of Acetoacetylated Celluloses, *CAA*

The first literature report about acetoacetylation of Cellulose was by P. J. Wiezevich and A. H. Gleason from 1937, they react cotton linters with Diketene using sulfuric acid catalyst, but the product properties were not reported [5].

The report from H. Hagemeyer described that acetoacetylation of cellulose esters such as cellulose acetate and cellulose acetate propionate with Diketene. He showed that it is possible to obtain cellulose acetate acetoacetates with a degree of substitution, *DS*, higher than 1, who are already cross-linked by formalin and alkali [6].

Other kind of literature and very important to the development of the Synthesis of *CAA* was from H. Staudinger and T. Eicher. They employing a heterogeneous system of regenerated cellulose acetic acid with sodium acetate catalyst and they used Diketene as a reagent. They were able to obtain a product with a higher degree of substitution, *DS*, close to 3 the *DS* which was confirmed with Elemental Analysis. The product was soluble in acetic acid and acetone [7].

More recent works in this area has shown us that Cellulose can be dissolved in a combination of Lithium Chloride (LiCl) with amides such as N,N–Dimethylacetamide (DMAC) or 1-Methyl-2-Pyrrolidinone (NMP) [8,9].

With these solvent systems it is possible to syntheses cellulose acetoacetates under homogenous conditions. The Cellulose is dissolved in DMAC and LiCl, and then reacted with Diketene. This is the only published method available for synthesis of *CAA* with higher and lower degree of substitution. The solubility of the products depends on the value of *DS* and Nuclear Magnetic Resonance (NMR), Infrared (IR) and Elemental Analysis was used to characterize the final product obtained [10, 11].

The modification of cellulose can be carried with homogenous and heterogeneous reaction where the big difference of both is that the heterogeneous reactions conserve part of the fiber structure but in the homogenous reaction the fiber structure is destroyed.

2.2 Synthesis of Acetoacetylated fibers, C_fAA

Relative this important development it, don´t exist a lot of invention in this area. Making Acetoacetylated fibers with polymeric materials can get some good properties such as greater strength and stiffness. A great example is incorporated in glass fibers with polypropylene molding resin, which can produce a strong composite with different applications.

A big development in this area starts with K. Boustany and A. Y. Coran from 1976 with the preparation of a composite of a polymer matrix reinforced with cellulose fiber. The pretreatment of the fiber with polymeric material to reduce fiber-to-fiber interaction prior to incorporating it into the matrix aids dispersion and became with great properties of the composites. More than the pretreatment of the fiber and mixing this fiber into a polymeric matrix on a big or small scale are demanding of both time and equipment [12, 13].

The report of P. Hamed from 1976 also makes development in the treatment of the fibers for the manufacture of composites of discontinuous fiber and a polymer matrix. Another very important aspect of this development is the processes for preparing improved treated cellulose fibers [13].

Coran et al. from 1982 has continued the developments of composites of discontinuous cellulose fibers by mixing with methylol phenolic modified polyolefin and a bonding agent. His invention has practically important aspect that is the novel composites consist essentially from 2 to 55 weight percent of discontinuous cellulose fibers. The rest of 98 to 45 weight percent being a matrix comprising from 2 to 99 parts by weight of a methylol phenolic-modified crystalline polymer having 2-4 carbons atoms [14].

It has also been important the treatment of the fibers because it says that the parts modified of cellulose can reduce fiber-to-fiber interaction up to about 85 parts by weight per 100 parts of fibers by weight having useful properties [14].

3 Experimental Part

3.1 Synthesis of Cellulose Acetoacetates

The Synthesis of Cellulose Acetoacetates was performed for homogeneous and heterogeneous reaction with two different kinds of reagents. For each reagent was two experiments done, one for high and another for lower degree of substitution. This chapter will explain briefly how the experiment was performed to the Synthesis of Cellulose Acetoacetates.

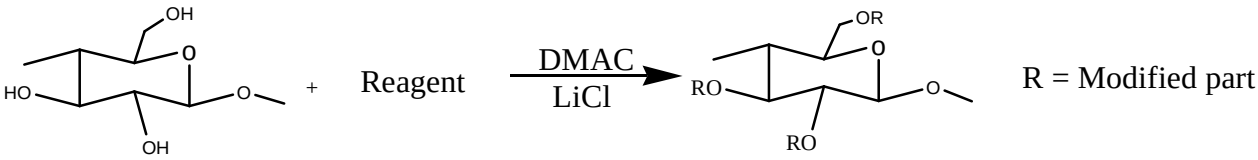


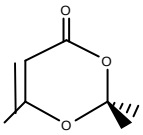
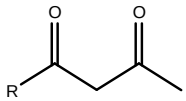
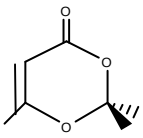
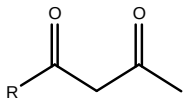
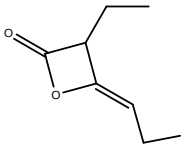
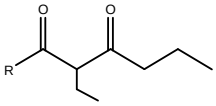
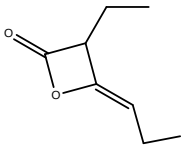
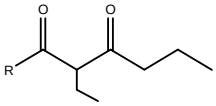
Figure 3: *Synthesis of Cellulose Acetoacetates for homogeneous reaction.*

Microcrystalline cellulose (MCC) was added to N,N–Dimethylacetamide (DMAC) and heated to 150 ºC during 26 min. After that was Lithium Chloride (LiCl) added and heated to 150 ºC during 8 min. Distillation to remove water under reduced pressure and then the reaction mixture was cooled to room temperature to obtain a clear solution of Cellulose dissolved in DMAC/LiCl [10].

The mixture was heated to 100 ºC and after that the reagent was added to the cellulose solution slowly. The different between the two reagents is that with the 2,2,6-Trimethyl-4H-1,3-dioxin-4-one (Diketene Analoge) the solution was heated to 100 º C during 40 min to evaporate the acetone [11] whereas for the 3-Ethyl-4-propylideneoxetan-2-one (Ethylketene Dimer) [15, 16] was the same procedure but where no acetone evaporating. Both of the solution became brown liquids and upon addition of reagent where stirred until reach room temperature [10].

In the ***Table 2*** is represented the quantities of all of the reagents used in the experiments for low and high degree of substitution and the respective modification part of the cellulose. For the reaction of high degree of substitution was 100 mmol of reagent used and for low degree of substitution was 44 mmol of reagents used.

Table 2: *Quantities used in all of the homogeneous reaction.*

Experiment	Reagent [11, 15, 16]	n_{MCC} (mmol)	V_{DMAC} (ml)	m_{LiCl} (g)	$n_{reagent}$ (mmol)	Modified Part
1		24,65	150	7,5	100	
2		24,65	150	7,5	44,4	
3		24,65	150	7,5	100	
4		24,65	150	7,5	44,4	

As reference experiment a reaction without any reagent but only dissolved Cellulose was performed. This was done to compare the results with the other experiments.

When the reaction was complete Ethanol was added to precipitate out the product was stirred for a couple of hours. Thereafter was the Cellulose filtered and left drying for a couple of days. ***Figure 4*** shows *a)* the evaporation part of the Acetone and *b)* the precipitate of the cellulose with Ethanol.

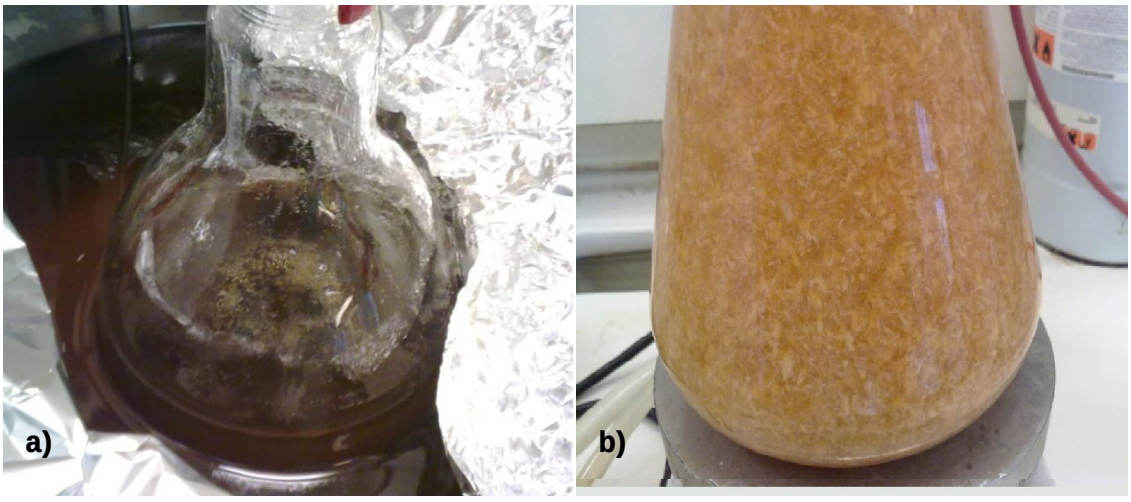


Figure 4: a) *Evaporation of Acetone;* ***b)*** *Precipitation of Cellulose.*

Then the samples were putted in Acetone and left stirring for a while to see if some part of the sample was, or not, soluble in Acetone. A small piece of the sample was dried in oven over night before infrared spectroscopy and sent to the *Mikroanalytisches Laboratorium KOLBE* in Germany to obtain the results of Elemental Analysis, EA, for the percentage of carbons. In the next table are the weight and the results of Element Analysis of which samples obtained.

Table 3: *Weights and Elemental Analysis results for the sample of homogeneous reaction.*

Experiment	MCC initial	MCC modified		Soluble Acetone		Not Soluble in Acetone		Kept
	m (g)	m(g)	EA (%)	m (g)	EA (%)	m (g)	EA (%)	m (g)
1	4,0	9,7586	48,90	0,9415	49,90	5,7109	47,50	1,0255
2	4,0	6,4000	46,37	0	------	4,9736	45,10	1,0416
3	4,0	7,4821	52,32	2,9097	55,29	1,1970	48,70	1,6181
4	4,0	5,4055	46,33	0	------	2,7750	45,02	1,5258
5	4,0	6,9336	37,23	0	------	5,0852	34,03	1,0110

Is important to refer that was kept about one to two grams of all the samples, for future work in compounding composites with polyethylene. Most of the experiment don´t reach the same value of weight after the reaction because different amounts of reagent have been used and the reagent used has different reactivity.

The next type of reaction is a heterogeneous reaction to Synthesize Cellulose Acetoacetates with the same type of reagents used for homogenous reaction but with a different solvent system. ***Figure 5*** represents the reaction for heterogeneous reaction.

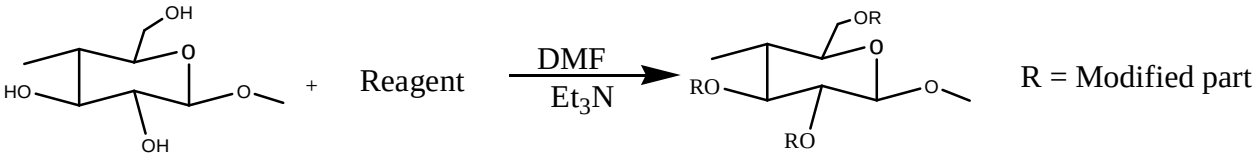
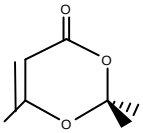
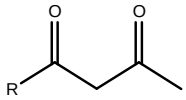
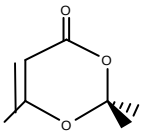
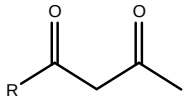
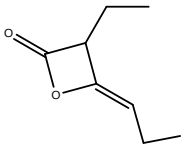
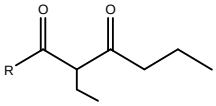
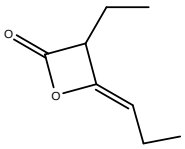
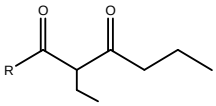


Figure 5: *Synthesis of Cellulose Acetoacetates for heterogeneous reaction.*

First a flask was purged with Nitrogen (N_2) (g) for a few minutes and then was N,N-Dimethylformamide (DMF), Triethylamine (Et_3N) and MCC added in the flask in named order. The mixture was stirred and heated to 115 ºC during a couple of minutes and after that was the reagent added. The N_2(g) was removed after a few minutes and the reaction flask was

closed. The mixture was kept stirring at 115 ºC for 6 h and after that the mixture was allowed to cool for 30 minutes. The mixture was filtered through a Buchner funnel with filter paper [17]. In ***Table 4*** the quantities of reagent and solvent used in the procedures can be found.

Table 4: Quantities used in all of the heterogeneous reaction.

Experiment	Reagent [11, 15, 16]	n_{MCC} (mmol)	V_{DMF} (ml)	V_{Et3N} (ml)	$n_{reagent}$ (mmol)	Modified Part
6		18,49	150	7,78	55,47	
7		18,49	150	7,78	18,49	
8		18,49	150	7,78	55,47	
9		18,49	150	7,78	18,49	

As for the homogeneous reaction a reference experiment not specified in ***Table 4*** was performed with only Cellulose without adding reagent but the procedure was the same like the others experiments. During the heterogeneous reaction, it was observed that during the reaction time it became a homogeneous solution.

After the reaction the mixture was worked up, it was washed and filtered with DMF, Ethanol, Acetone, Ethanol and Water and let it dried for a couple of days. A solubility test was made on all of the samples but no soluble part was found in solvents.

A small sample was dried in oven over night before infrared spectroscopy and sent to the *Mikroanalytisches Laboratorium KOLBE* in Germany to obtain the results of Elemental Analysis for the percentage of carbons. In the ***Table 5*** are the weight and the results of Element Analysis of the samples.

Table 5: *Weights and Elemental Analysis results for witch sample of heterogeneous reaction.*

Experiment	MCC initial	MCC modified / weight (g)	MCC modified / EA (%)
6	3,0	1,1623	44,26
7	3,0	0,9448	43,53
8	3,0	3,1793	53,67
9	3,0	2,1095	44,40
10	3,0	2,0847	44,82

In ***Figure 6*** are all of the samples after the homogeneous and heterogeneous reaction shown.

Figure 6: *Final result of all the homogeneous and heterogeneous reactions.*

The sample of homogeneous reaction is represented in the first line, *Exp. 1-5,* bellow is the heterogeneous reactions, *Exp. 6-10,* it can be seen that the heterogeneous samples are more powder then the homogeneous.

3.2 Compounding Composites of Cellulose Fibers

In this experimental part of my project Cellulose fibers, from the homogeneous and the heterogeneous reactions, where blended with polyethylene to investigate the proprieties.

For this experiment polyethylene (920 Kg/m^3 bmp: 100-140 ºC) with the different kinds of modified cellulose. The part of cellulose obtains in homogeneous a reaction that was soluble in Acetone (SA) or not (NSA) was also tested. The machine used for the compounding the composite was a *HAAKE Minilab Rheomex CTW5 is* represented in the figure below.

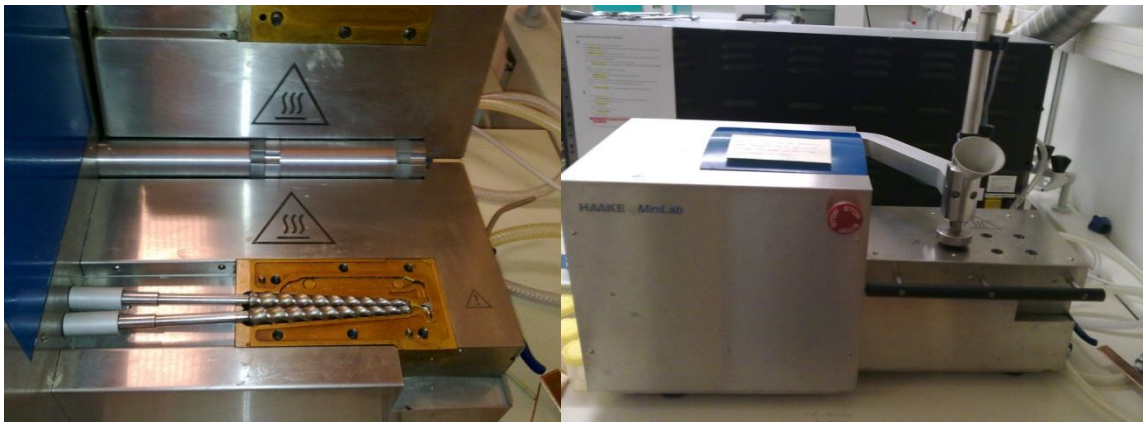


Figure 7: *Extruder - HAAKE Minilab Rheomex CTW5.*

In ***Table 6*** is represented the operation conditions of all the procedure.

Table 6: *Operation Conditions used in the extruder in all the experiences.*

Cellulose Modified (g)	Polyethylene (g)	T (ºC)	N (rpm)	t (min)
0,32	2,88	150	60	10

The ***Table 7*** describes all the values giving by the extruder of each sample. In the table the experiment between 1 and 10 are the experiment made in heterogeneous and homogeneous reaction. The experiment 5 was not made because was very difficult to make a powder.

Table 7: *Values received by the extruder of homogeneous, 1-5, and heterogeneous, 6-10.*

Exp.	m_{final} (g)	ΔP (bar)	M (Ncm)	$\mu \times 10^3$(Pa.s)	Exp	m_{final} (g)	ΔP (bar)	M (Ncm)	$\mu \times 10^3$(Pa.s)
1	1,04	8,5	32	3,70	**7**	0,91	11	40	4,80
2	1,31	10,0	36	4,50	**8**	1,35	-------	-------	-------
3	0,96	7,5	28	3,25	**9**	1,03	11	34	4,30
4	1,03	4	28	1,90	**10**	0,95	10	35	4,45
5	-------	-------	-------	-------	**MCC**	0,85	7	26	3,25
6	1,34	13	36	5,65	**PE**	0,93	7	24	4,23

Like was refer in the homogeneous reaction we can see that was possible to see that in some experiment we obtain some modified MCC soluble in Acetone or not with different EA. Then we consider important to test this experiments with polyethylene to see if the results of the composites are different to the others represented in the ***Table 8***.

Table 8: *Values receive by the extruder of soluble or not in Acetone.*

Exp.	m_{final} (g)	ΔP (bar)	M (Ncm)	$\mu \times 10^3$(Pa.s)
1 – SA	0,60	6	40	2,75
1 - NSA	-------	-------	-------	-------
2 - NSA	1,03	-------	-------	-------
3 - SA	1,30	10	34	4,4
3 - NSA	1,26	13	34	5,4
4 - NSA	0,95	4	32	1,7
5 - NSA	0,94	7	29	2,9

All of the values represented in the ***Tables 7*** and ***8*** represent the average giving by the extruder not referring to the mass. One important value to analyze is the viscosity (μ) because is possible to see big different between all the samples and is significant to the characteristic of the material. The *Exp. 1-NSA* was not perform because very hard the material to make a powder and some was not possible to note the values.

In ***Table 8*** the results from the acetone soluble and non-soluble fractions can be found.

4 Results and Discussion

4.1 Characterization of CAA by Infrared Spectroscopy

The comparison of the IR spectra of modified CAA and MCC (unmodified Cellulose) gives information of the product outcome. The modification should give a new ester carbonyl band (at 1715-1750 cm^{-1}) and an increase in the intensity of the alkanes band (at 2800-3000 cm^{-1}). Furthermore the intensity of the alcohols in cellulose band (at 3200-3500 cm^{-1}) should decrease. This three areas in the IR spectra are the most important to see and to prove the modification in Cellulose.

In the beginning we will start to show and compare the results from the homogeneous reactions with the same nomenclature used in the experimental part in the ***Table 2*** and ***3***. The spectra's that will appear during this chapter aren´t all in the same scale but all will be explained. In the first two experiments we compare with MCC because these two experiments differ only in the quantity used of the reagent (Diketene Analoge) represented in ***Figure 8***.

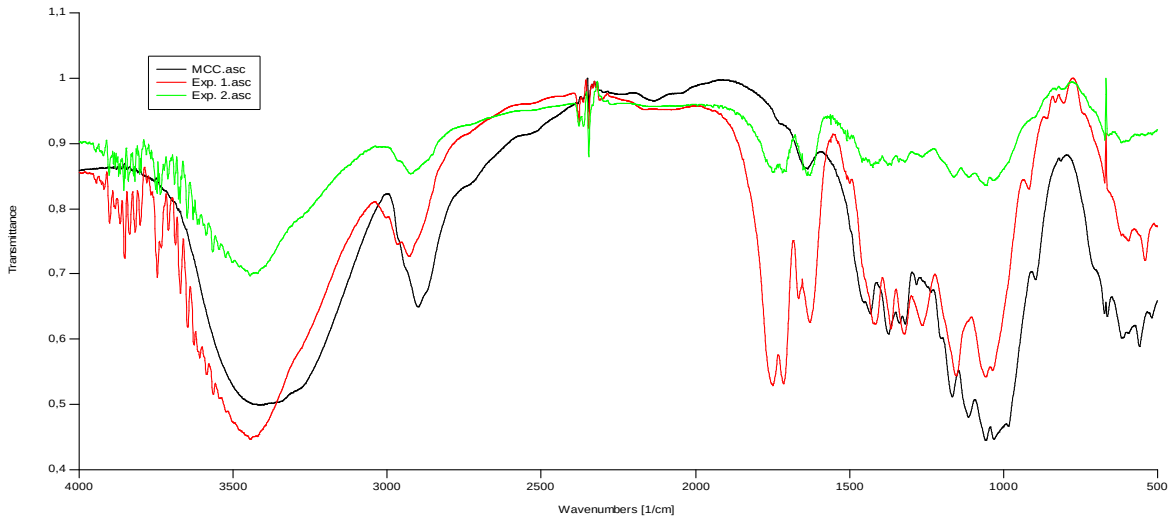


Figure 8: *IR spectrum comparing MCC with modified Cellulose with Diketene Analoge for homogeneous reaction.*

In this figure we can say that in both of the experiment the reaction occurs because it is possible to see difference in the alcohol, ester carbonyl and alkanes bands. The *Exp. 1* was to obtain high *DS* and comparing with the *Exp. 2* (low *DS*) we see that the strength of the ester carbonyl band is larger in the *Exp. 1*.

In ***Figure 9*** is represented for homogeneous reaction like the other but using the reagent Ethylketene Dimer.

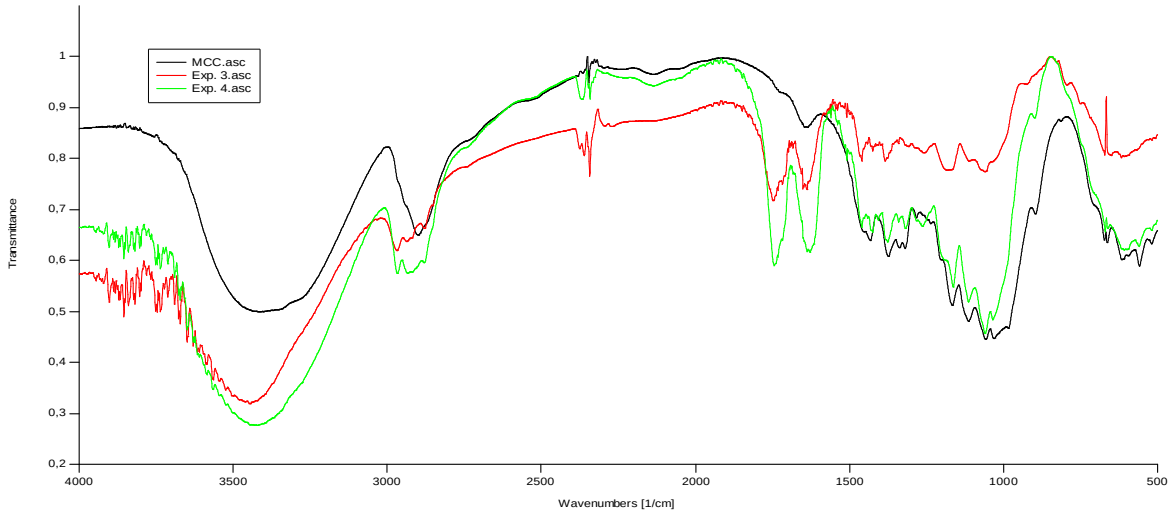


Figure 9: *IR spectrum comparing MCC with modified Cellulose with Ethylketene Dimer for homogeneous reaction.*

In this figure both of the experiment changed the Cellulose because of the same reasons of the explained for the ***Figure 8***. The large difference seems to be how strong the band of ester carbonyl, that in this case seem to be stronger in the Exp. 4 (low *DS*) but the scale is not really the same. If compare in the *Exp. 3* the peak between 1660-1750 cm^{-1} are then the band at 1000-1500 cm^{-1} something big different comparing with the *Exp. 4*. Then the *Exp. 3* should have a high *DS* comparing with *Exp. 4*.

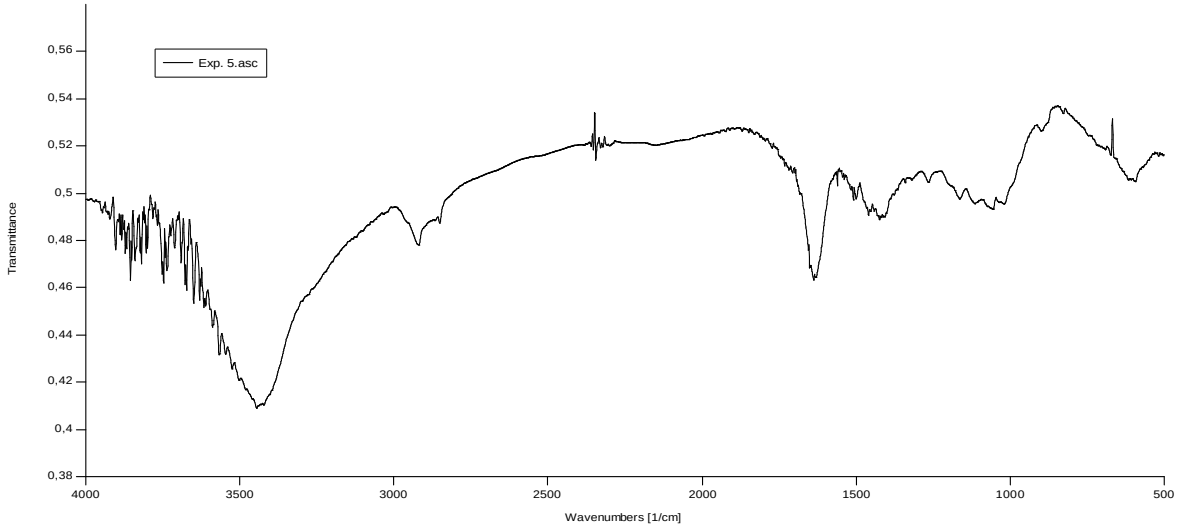


Figure 10: *IR spectrum with dissolving Cellulose without reagent for homogeneous reaction.*

The next evaluation is on the MCC reference with Cellulose dissolve only in DMAC without adding any reagent. In ***Figure 10*** is the IR spectrum shown at the reference MCC and in the spectra the ester carbonyl band and the alkanes bands are not represented.

After this analysis the ***Figure 11*** compare with different reagents used in the synthesis of CAA.

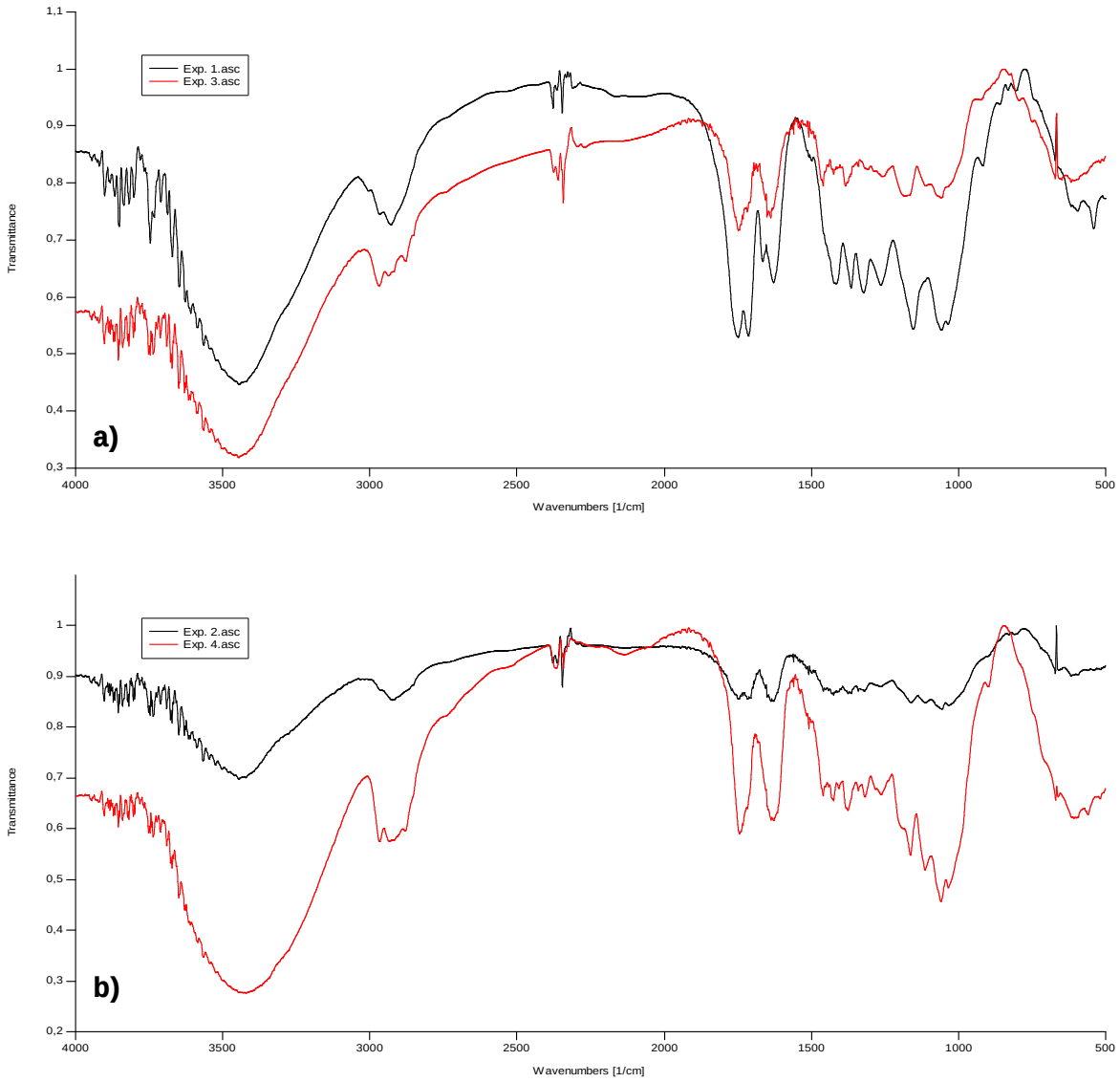
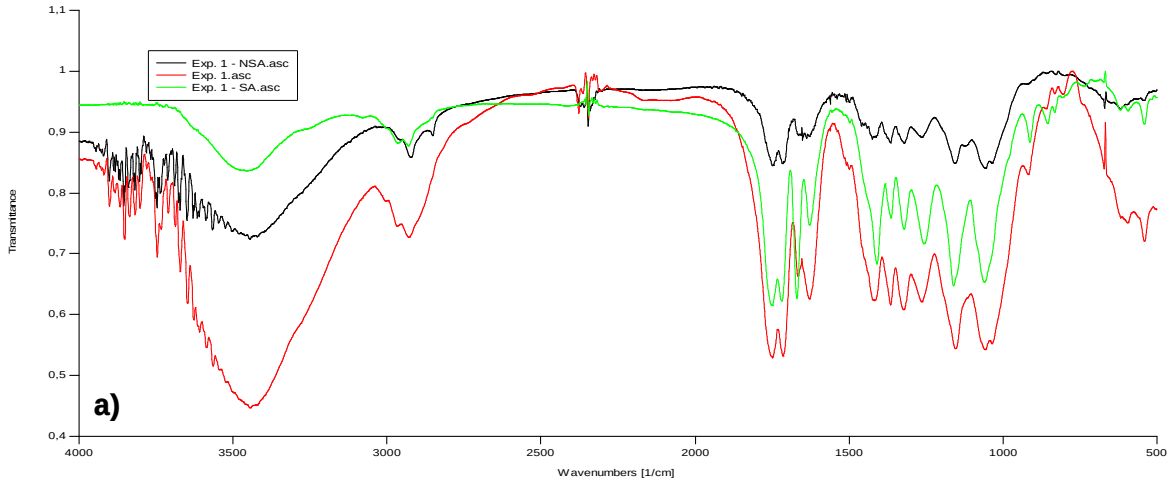
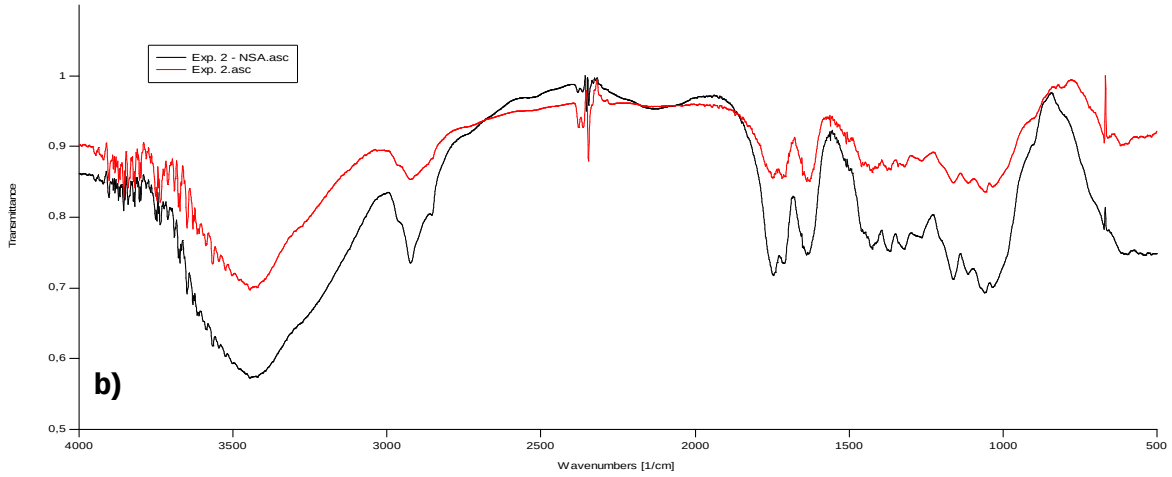


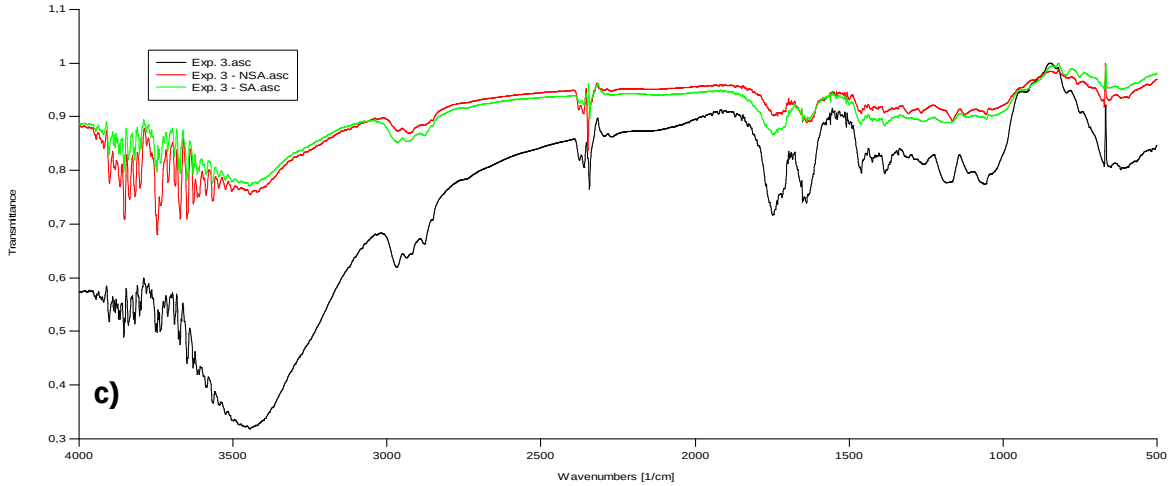
Figure 11: *IR spectrum with different reagents for homogeneous reaction – a) High DS; b) Low DS.*

In ***Figure 11-a)*** is probable that the *Exp. 3* with the Ethylketene Dimer have a bigger DS than with the Diketene Analoge because the peak from the ester carbonyl band is stronger comparing to the peak between at 1000-1500 cm^{-1}. In the case of ***Figure 11-b)*** it seems to have the *Exp.2* more DS than the *Exp. 4* but is very difficult to say because in both of the figures the experiences aren´t in the same scale.

For the homogeneous reaction we investigated the solubility in Acetone at the product and were possible to see that we obtain after the reaction part some part soluble in Acetone or not. It was concluded that material with high *DS* is soluble in Acetone and the inverse for low *DS*. In ***Figure 12*** is represented the entire test with Acetone of the homogeneous samples.


Exp. 1 - NSA.asc
Exp. 1.asc
Exp. 1 - SA.asc
Transmittance
Wavenumbers [1/cm]
a)


Exp. 2 - NSA.asc
Exp. 2.asc
Transmittance
Wavenumbers [1/cm]
b)


Exp. 3.asc
Exp. 3 - NSA.asc
Exp. 3 - SA.asc
Transmittance
Wavenumbers [1/cm]
c)

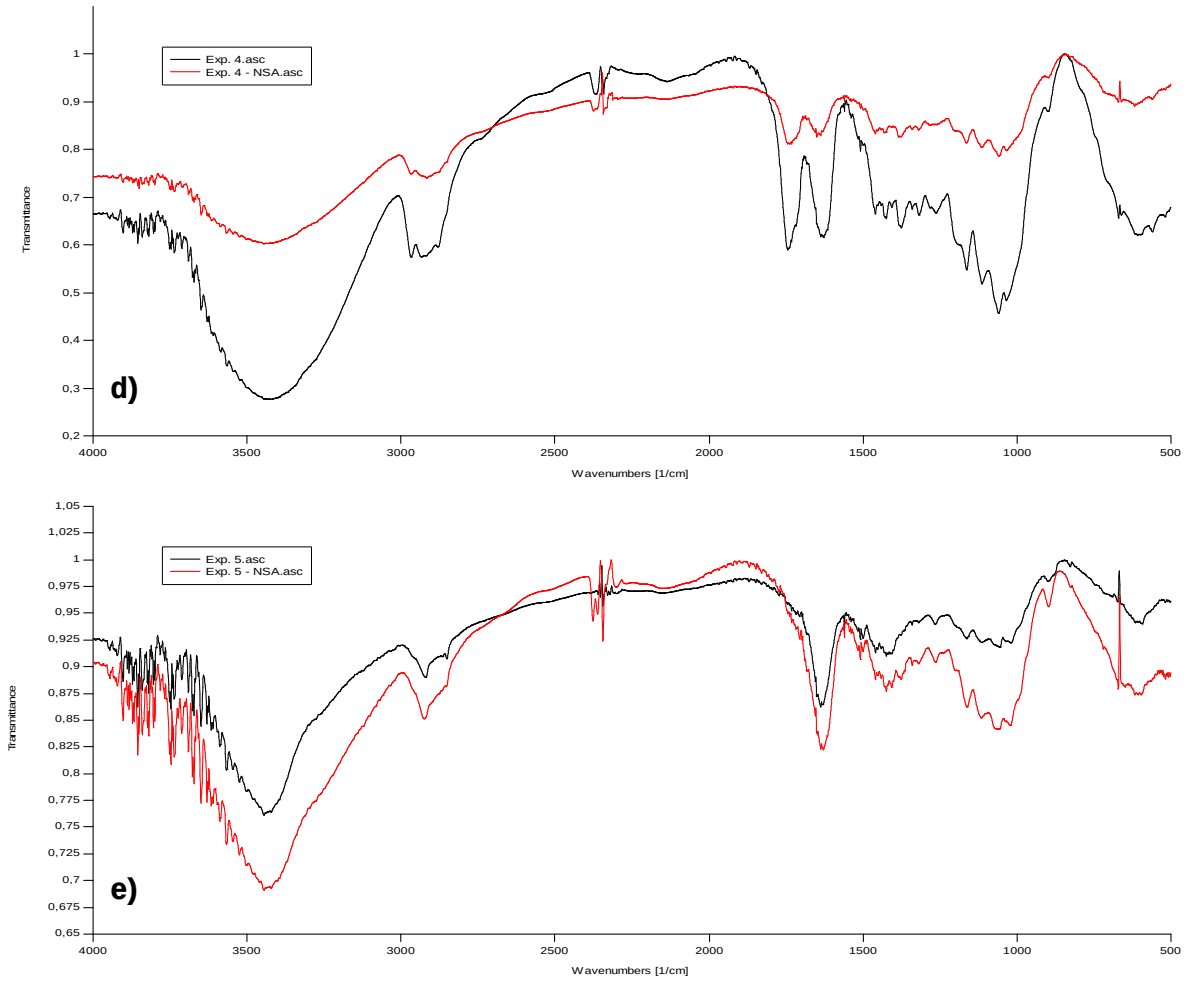


Figure 12: *IR spectrum's of soluble test for homogeneous reaction – a) Exp. 1; b) Exp. 2; c) Exp. 3; d) Exp. 4; e) Exp. 5.*

Summarizing all the spectra's we see that in all of the experiments except *Exp. 5* show some modification part in cellulose that means that we have some *DS* in all of the sample.

Something important to refer for the homogeneous reactions is the time of reaction. The time is important to see if cellulose modified depending on the time and that is relevant. In all of the experiments discussed in this chapter the time of reaction was 40 minutes and we observe in the spectra´s this change. In this project was tried to do a time of reaction of 12 hours and running an IR spectra and in the end the sample are the same like the starting material.

The next part in the characterization by IR is the heterogeneous reaction. First the same reagents with different quantities will be compared and then with different reagents with the same quantities. In ***Figure 13*** is represented with Diketene Analoge but for high and low *DS*.

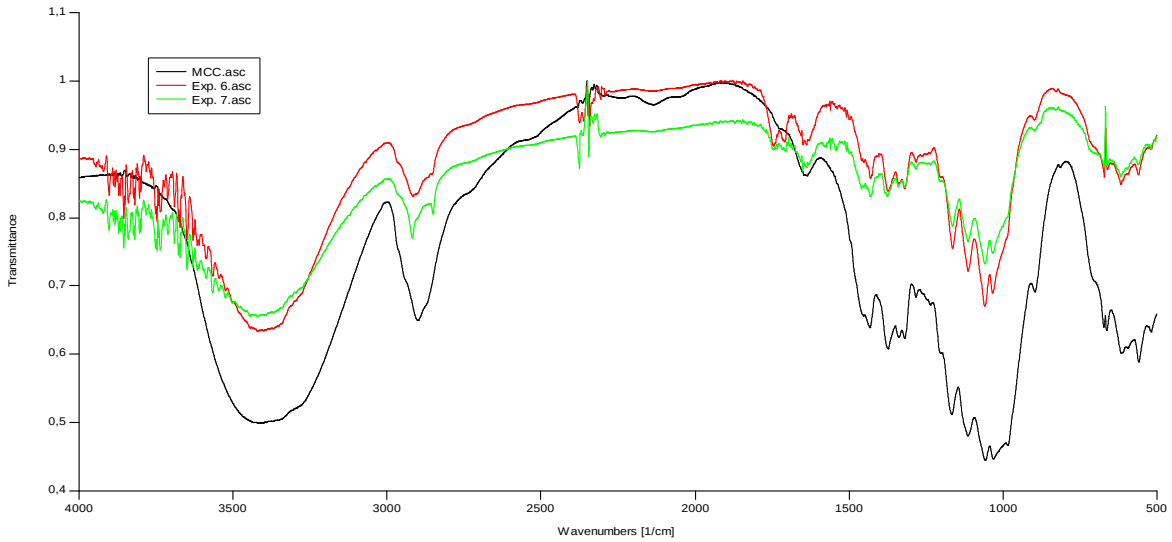


Figure 13: *IR spectrum comparing MCC with modified Cellulose with Diketene Analoge for heterogeneous reaction.*

In the analysis of the figure above we can see that some small peaks in the ester carbonyl band appear and alkanes band too. Comparing only the two experiments is possible to say that *DS* from both is very small. This means that we can modify Cellulose with a heterogeneous reaction with high and low *DS* with Diketene Analoge. One explanation to the low *DS* is that in heterogeneous reactions the fiber is kept almost intact and mainly the surface can be modified.

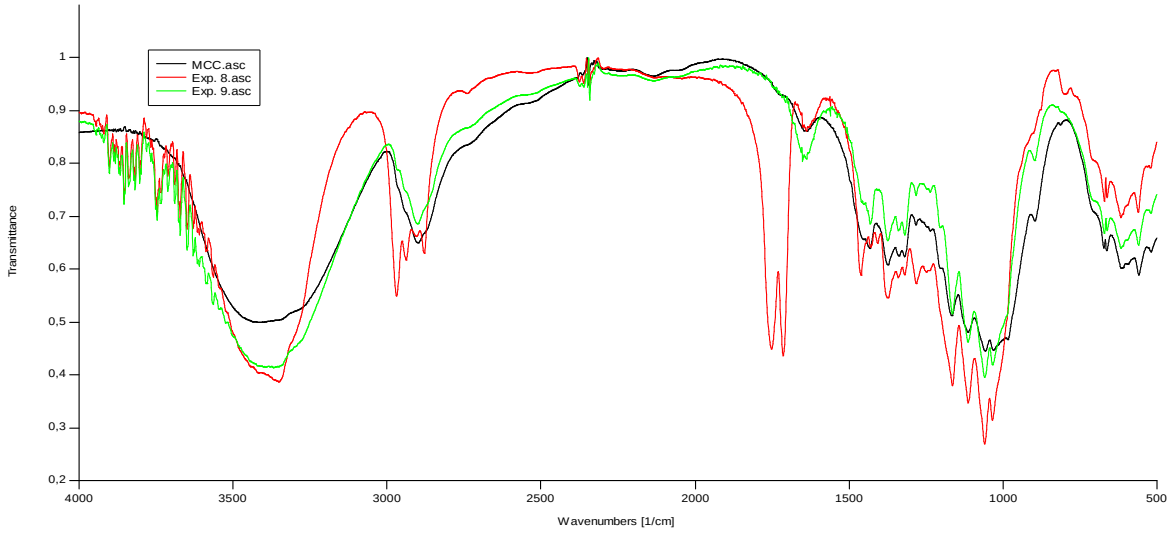


Figure 14: *IR spectrum comparing MCC with modified Cellulose with Ethylketene Dimer for heterogeneous reaction.*

In the figure above is the represented the experiments with the Ethylketene Dimer with MCC. As can be seen in the figure only Exp. 8 modifies the Cellulose, this was with test with high *DS*. The *Exp. 9* is practically the same like MCC then this experiment didn´t react

with the amount of reagent used. The difference in the ester carbonyl band and the alkanes is very significant to observe for the test of high *DS.*

The next point analyzes the reference MCC, with MCC dissolved in solvents without adding any reagent in ***Figure 15.***

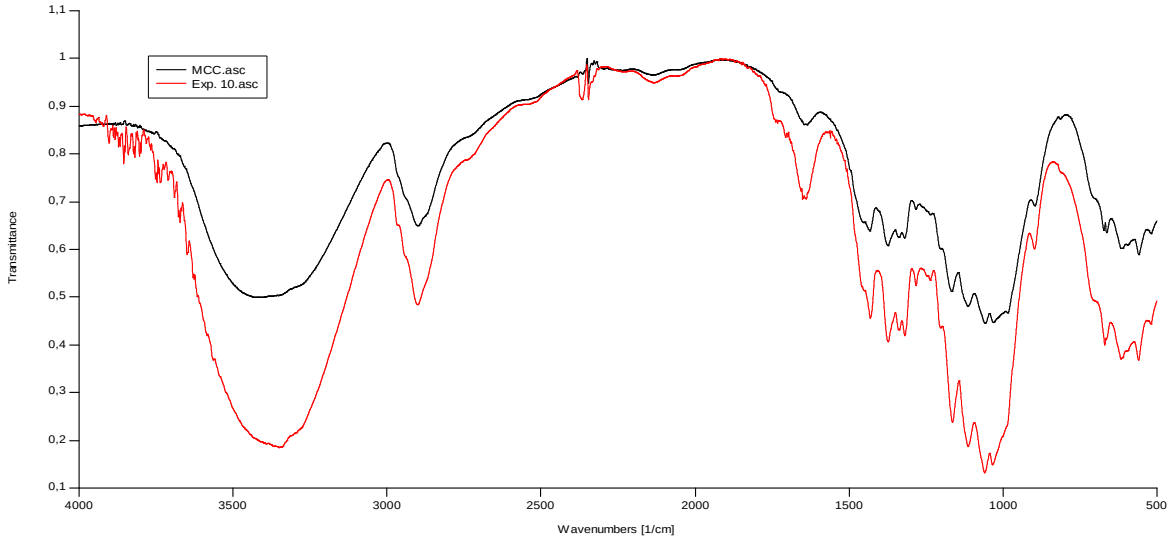


Figure 15: *IR spectrum with dissolving Cellulose without reagent for heterogeneous reaction.*

The results are the same for homogeneous reaction where we observe that dissolving Cellulose in solvent gives on IR that is practically the same as pure MCC.

The last part was to compare different reagents at the same quantities. ***Figure 16*** represented the two reagents for high *DS* this results and is possible to see some different.

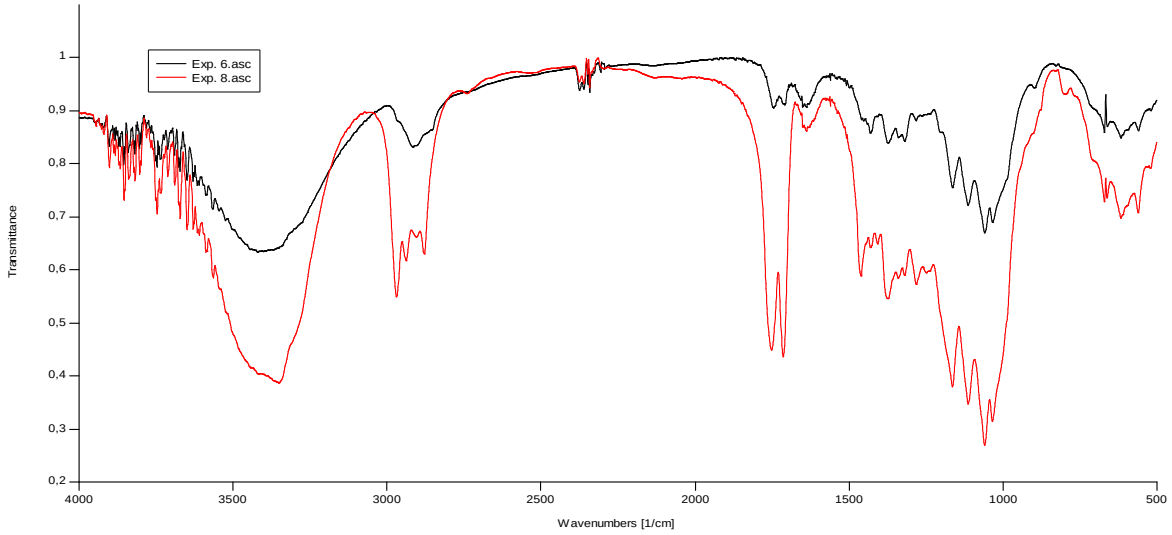


Figure 16: *IR spectrum with different reagent with high DS for heterogeneous reaction.*

Looking in the figure above there is a significant difference in the alkanes bands which is expected because the modified part of cellulose with the Ethylketene Dimer (*Exp.* 8) have more C-H connection. Therefore the peak for alkane should be stronger then with Diketene

Analoge (*Exp. 6*). More interesting is that the carbonyl group in *Exp. 8* is relatively stronger than the carbonyl group in *Exp. 6*. This indicates that Ethylketene Dimer is more reactive than the Diketene Analoge.

For the case of low *DS* the spectra will not be presented because for low *DS* with Ethylketene Dimer (*Exp. 9*) nothing react with reagent being impossible to obtain some modified Cellulose.

As last part in this section the homogenous reaction will be compared with heterogeneous reaction using the same reagent and quantities. First the ***Figure 17*** represents for high and low *DS* with Diketene Analoge.

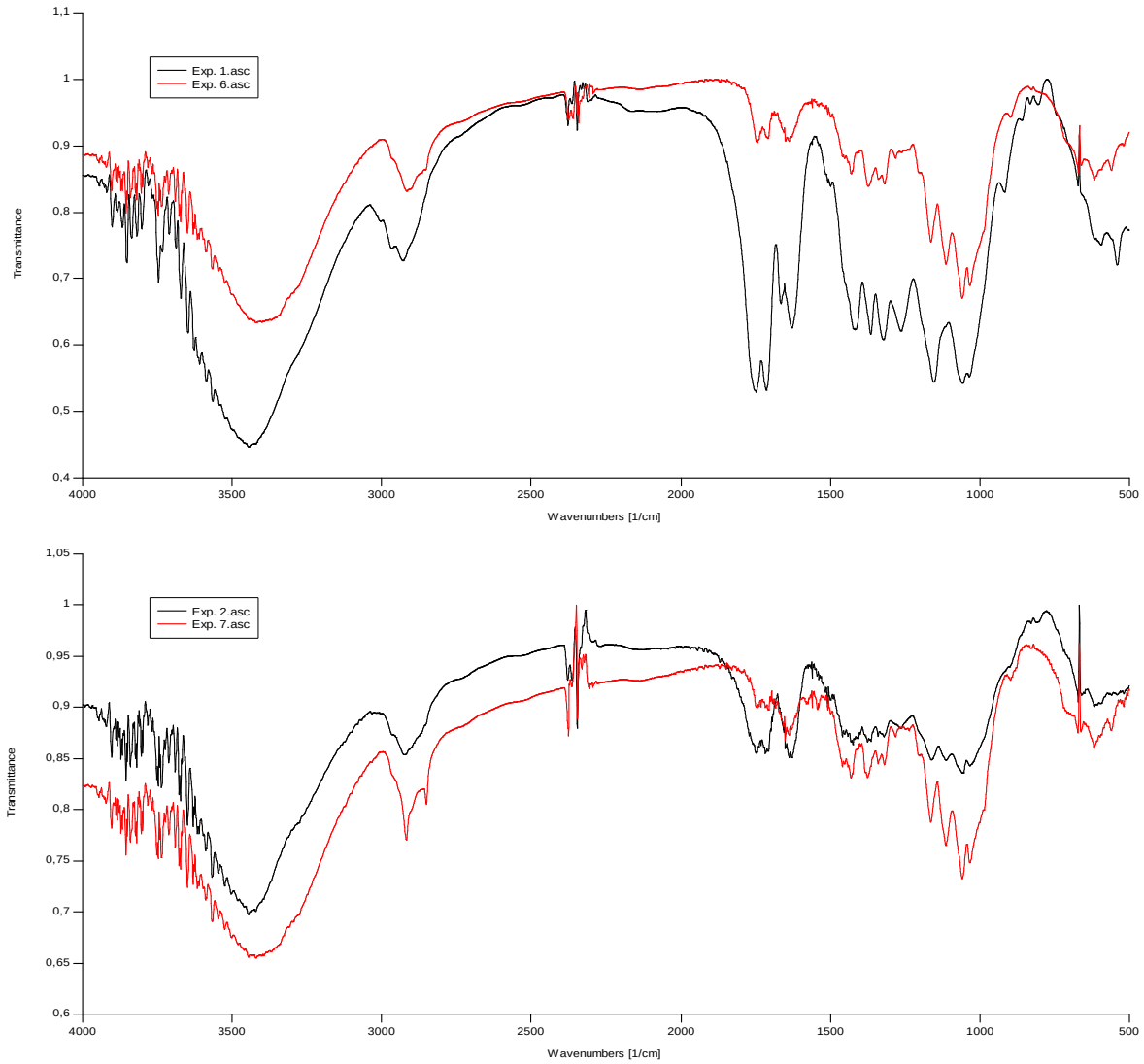


Figure 17: *IR spectrum´s with Diketene Analoge in different reaction.*

If we look for the both spectra´s of Figure 17 is possible to see that in the alkanes band is stronger in the homogeneous reactions then the heterogeneous and this is because in the homogeneous the cellulose is dissolve in totally in the solvent that permit extend all the Cellulose fiber. This procedure makes it easier to make the Cellulose to react with the

reagent. The probability to obtain a high *DS* in the homogeneous reaction is higher than for heterogeneous reaction.

In the case of Ethylketene Dimer shown in the figure below it is possible to say that the peaks are more evident in the heterogeneous reaction *Exp. 8* compared to the ones in homogeneous reaction. The alkanes peaks are bigger comparing with the peaks at 1000-1500 cm^{-1}. From the intensities of peaks it can be conclude that the material from *Exp. 3* has higher *DS* then the other experiments.

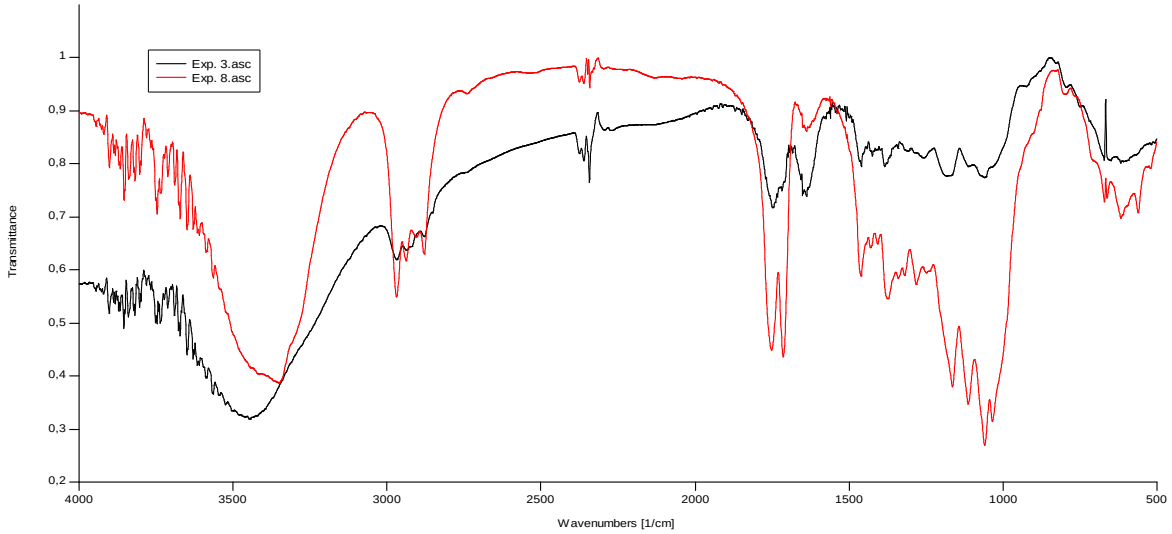


Figure 18: *IR spectrum with Ethylketene Dimer in different reaction.*

For the reactions with low *DS* no comparison will be done since with we have already seen that in the heterogeneous reaction nothing react on the Cellulose. Looking to all the spectra´s we can tell some about the results but we the EA results will give more results. In both types of reaction with Cellulose the supramolecular structure of Cellulose is completely destroyed and the original physicomechanical properties of the Cellulose are lost. The conditions used during the procedure are very important because if not all hydroxyl groups are accessible for reaction the modification can only occur at the fiber surface.

4.2 Characterization CAA by Elemental Analysis

In this part of the results we will determine the *DS* for the modified Cellulose. In this case we know that the formula for the calculation is different for the two different reagents used for the synthesis. First for the Diketene Analoge the cellulose ester has the follow molecular formula [18]:

$$C_{6+\sum DS\cdot n}H_{10+\sum DS\cdot n}O_{5+\sum DS(n-2)},$$

where the *DS* is the degree of substitution and *n* the number of carbon atoms in the substituent. From the molecular formula is possible to establish equations for carbon (***C***), hydrogen (***H***) and oxygen (***O***) expressed as a fraction [18].

$$\boldsymbol{C} = \frac{12{,}011\cdot(6+DS\cdot n)}{12{,}011\cdot(6+DS\cdot n)+1{,}008\cdot(10+DS\cdot n)+15{,}999\cdot\left(5+DS(n-2)\right)} \quad (4.1)$$

$$\boldsymbol{H} = \frac{1{,}008\cdot(10+DS\cdot n)}{12{,}011\cdot(6+DS\cdot n)+1{,}008\cdot(10+DS\cdot n)+15{,}999\cdot\left(5+DS(n-2)\right)} \quad (4.2)$$

$$\boldsymbol{O} = \frac{15{,}999\cdot\left(5+DS(n-2)\right)}{12{,}011\cdot(6+DS\cdot n)+1{,}008\cdot(10+DS\cdot n)+15{,}999\cdot\left(5+DS(n-2)\right)} \quad (4.3)$$

In these equations only two are independent the third equation is fixed by the intrinsic relation

$$\boldsymbol{C} + \boldsymbol{H} + \boldsymbol{O} = 1 \quad (4.4)$$

Then resolving this system with the equation (4.2), (4.3) and (4.4) using the EA values of carbon is possible to determine the individual *DS*-value in the next equation represented.

$$DS = \frac{72{,}066-162{,}141\cdot\mathbf{C}}{29{,}018\cdot\mathbf{C}\cdot\mathrm{n}-31{,}998\cdot\mathbf{C}-12{,}011\cdot\mathrm{n}} \quad (4.5)$$

For the case of Ethylketene Dimer molecular formula is different and is represented bellow

$$C_{6+\sum DS\cdot n}H_{10+\sum DS\cdot(n+4)}O_{5+\sum DS(n-6)},$$

with the same legend for the Diketene Analoge the equation of Carbon,

$$\boldsymbol{C} = \frac{12{,}011\cdot(6+DS\cdot n)}{12{,}011\cdot(6+DS\cdot n)+1{,}008\cdot\left(10+DS(n+4)\right)+15{,}999\cdot\left(5+DS(n-6)\right)} \quad (4.6)$$

$$\boldsymbol{H} = \frac{1{,}008\cdot(10+DS\cdot n)}{12{,}011\cdot(6+DS\cdot n)+1{,}008\cdot\left(10+DS(n+4)\right)+15{,}999\cdot\left(5+DS(n-6)\right)} \quad (4.7)$$

$$\boldsymbol{O} = \frac{15{,}999\cdot\left(5+DS(n-2)\right)}{12{,}011\cdot(6+DS\cdot n)+1{,}008\cdot\left(10+DS(n+4)\right)+15{,}999\cdot\left(5+DS(n-6)\right)} \quad (4.8)$$

Then resolving this system with the equation (7), (8) and (4) using the EA values of carbon is possible to determine the individual *DS*-value in the next equation represented [18].

$$DS = \frac{72{,}066 - 162{,}141 \cdot \mathbf{C}}{29{,}018 \cdot \mathbf{C} \cdot \mathrm{n} - 91{,}908 \cdot \mathbf{C} - 12{,}011 \cdot \mathrm{n}} \tag{4.9}$$

Using the equations (4.5) and (4.9) to calculate the *DS* for the different reagents is possible to show in the ***Table 9*** all of the homogeneous reaction with the same nomenclature used in the experimental part in the ***Table 2*** and ***3***.

Table 9: *DS values for the homogeneous and heterogeneous reactions.*

Experience	*DS*	*DS – Soluble in Acetone*	*DS – Not Soluble in Acetone*
1	1,05	1,45	0,61
2	0,34	-------	0,10
3	0,56	0,95	0,25
4	0,10	-------	0,03
5	-0,70	-------	-0,87
6	-0,03	-------	-------
7	-0.13	-------	-------
8	0,72	-------	-------
9	0,00	-------	-------
10	0,01	-------	-------

Starting to discuss the part of the homogeneous reactions it is possible to say that between the same reagents but with high and low amount of reagent we obtain higher *DS* with higher amount of reagent. In both case of the same reagents we see a big difference between. In the *Exp 1* and *2* the difference is three times bigger but for the *Exp. 3* and *4* the difference is five times. This is very important because it was not possible to obtain a very high *DS* for the *Exp. 1* and *3* but we know that is possible to obtain a big difference between the high and the low *DS* with these reagents. A plausible explanation to this is that the material in the end is very strong to break, like is demonstrate in the ***Figure 6***, and as a consequence there may be some water present in the middle of our sample that decrease the value of *DS*. In *Exp. 5* we observe a *DS* value negative, very strange, but this experience was only dissolving cellulose in the solvents. The supramolecular of Cellulose is completely destroyed when we dissolve the Cellulose, the original proprieties of the fibers.

For the homogenous reaction the solubility of the samples in Acetone also a small sample was sent to EA. In the text below it will be seen that some part is soluble in Acetone or not the *DS* value will be different and higher for the fraction that is soluble in Acetone. Can be seen by looking into to table, ***Table 9***, that in all the samples the part not soluble in Acetone has always lower *DS* than the ones soluble in Acetone. From this we can say that for a reaction it is possible to that are fractionate two fractions one with high and one with low *DS* by using an Acetone wash step.

For the homogeneous reactions it was necessary during the dissolving process to distill, remove the most part of water mixture. If some water stays present inside the mixture during the reaction there may be side reactions on the Cellulose, and as a consequence reducing the *DS* value.

For the heterogeneous reactions, *Exp. 6* to *10*, we can observe the two first experiments with negative value of *DS*. This is very strange since from the IR spectrum we observe carbonyl band, very small, but present in the samples. One explanation might be that the samples that were sending to EA contain water that decreases the value of *DS*. The *Exp. 8* has a *DS* of 0,72 something acceptable, and also IR confirms that a reaction has happened. Relative of the *Exp. 9* we confirm with IR spectra that the reaction with Ethylketene Dimer didn´t occur for the low *DS* and dissolving only the Cellulose in the solvent, *Exp. 10*, the value of the *DS* is practically zero, which it should be.

Comparing the two reactions with same quantities of reagent it can be seen in the table below that the *DS* values was higher for the homogeneous reaction compare to the heterogeneous. This is because in heterogeneous conditions not all of hydroxyl groups of the anhydroglucose units are available for the reactions as they are in the homogeneous reactions. The only experiments for this don´t occur was when comparing the Ethylketene Dimer for high *DS* where it was the opposite. Probably during the experimental procedure some mistakes were made.

4.3 Characterization CAA/Polyethylene Composites

To get some insight into the compatibility at the material with plastic material compounding to obtain composites between CAA and Polyethylene was done. The characterization in this chapter will only be qualitative. The technique used was of Dynamic Mechanical Analysis (DMA) which is a technique used to characterize materials viscoelastic behavior. Then by ocular observing only samples it is possible to see that some composites aren´t good and some have different proprieties compare to PE only.

In ***Figure 19*** is represented all the composites prepared including PE and MCC, the nomenclature used is the same as in ***Table 7*** and ***8.***

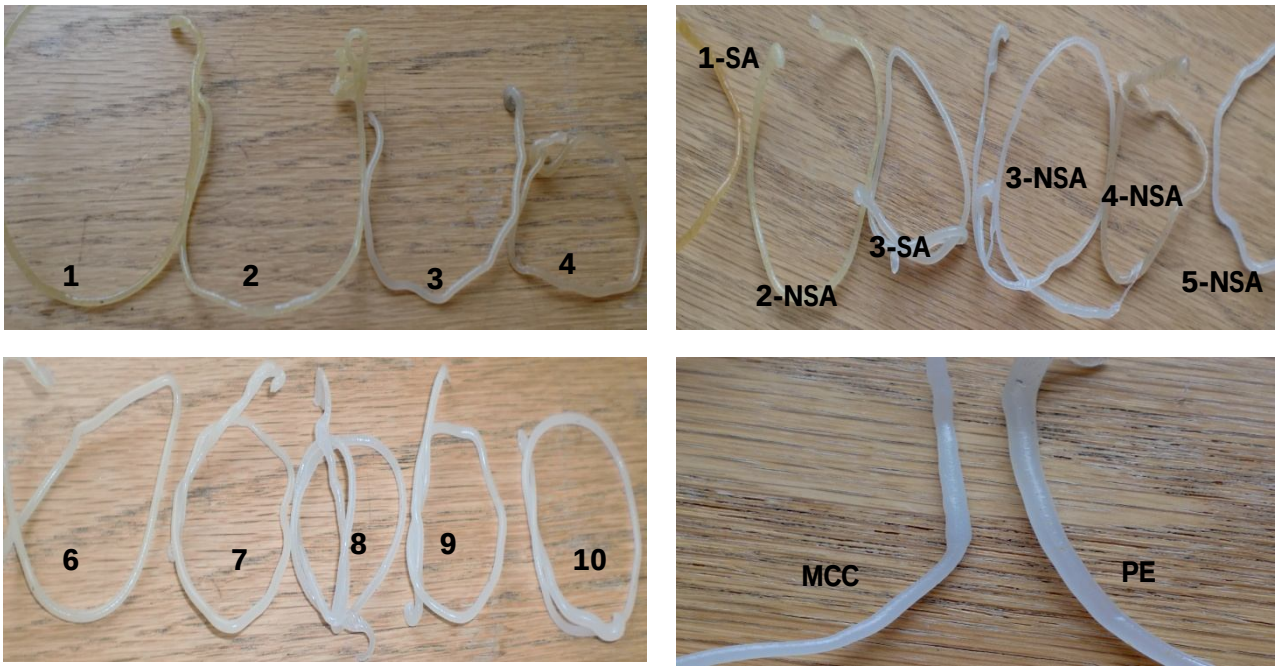


Figure 19: *Samples of the composites with PE.*

If we look only at the figure below a conclusion is that the color of the samples is similar compare to the pure PE. This observation is not really relevant because the color is relative to the reagent involving the Cellulose.

For some of the samples it was impossible to make the compounding due to the material. In ***Figure 20*** the difference between some materials are shown.

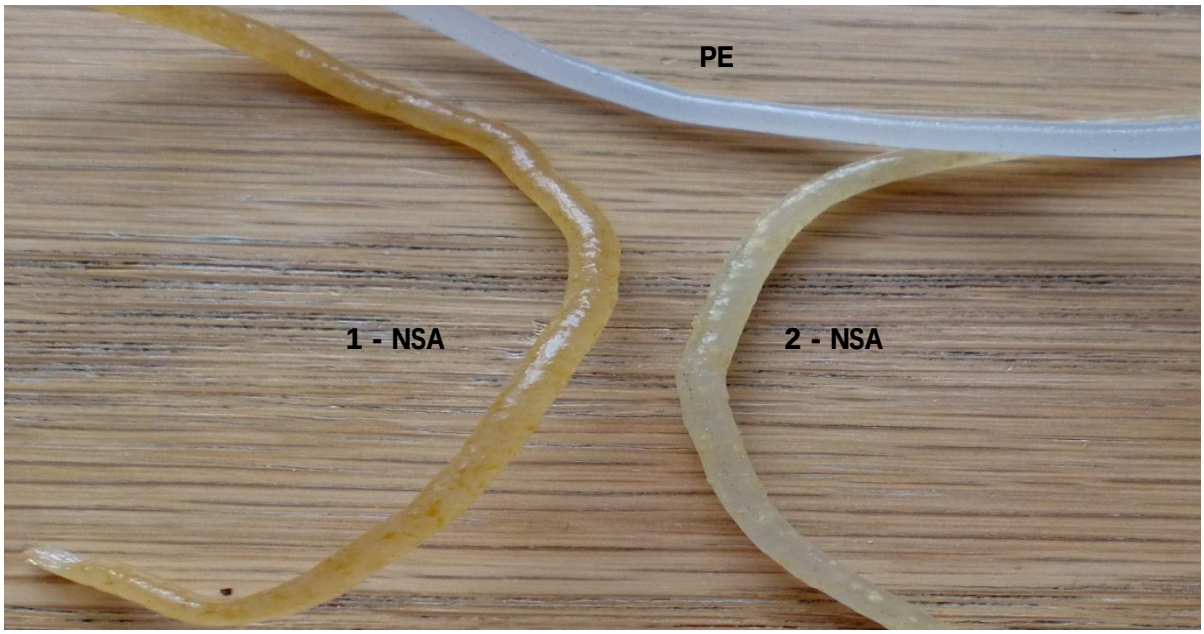


Figure 20: *Comparing Composites with Polyethylene.*

From the figure it is easy to observe that the two materials, *Exp. 1-NSA and 2-NSA*, have big solid material dispersed in the material. This tell us that these don´t make good composites. For all the composite material that we have investigated the samples from the homogeneous reactions are the ones that contains more solid material visual in our eyes. The composite material from heterogeneous reactions need further investigations with complementary equipments to be able to say if they are good or not.

5 Conclusions

In this project it was possible to make some conclusions. According to the IR it is possible to modified Cellulose, CAA, with different reagents Diketene Analoge and Ethylketene Dimer. By varying amount of reagent it was possible to obtain high and low *DS* for homogeneous as well as heterogeneous reactions. However for the reaction that should give low *DS* of Ethylketene Dimer no heterogeneous reaction on Cellulose occurred.

An important finding was that after homogeneous reaction product gave an Acetone soluble fraction. After we saw that some part of the material was soluble in Acetone or not, we were able to obtain a fraction with a narrower size distribution of DS. This was verified by the results receive by EA that the original sample of Cellulose modified has a value of *DS* between the part soluble and the not soluble in Acetone.

From the composites with PE there are very difficult to make some conclusions because not all characterization on the samples were done. It was possible to see that some composites don´t blend well with PE since some solid pieces disperses in the material and aren´t well mixed with PE.

6 Work Assessments

6.1 Aims Achieved

The proposal of this project was to make Cellulose Acetoacetates with different reagents and find if they can be freely shaped. Characterization of the material gives the Degree of Substitutions by Elemental Analysis and Infrared spectroscopy.

The second part of the project was to prepare Acetoacetylated fibers and characterization of the material by DMA.

6.2 Limitations and further work

A suggestion for further work is to analyze the composites made with polyethylene with the appropriate equipment, DMA, to give further insight in the proprieties of the composites. Another thing is to repeat the homogeneous and heterogeneous reaction, but with a different work up procedure and send to EA to see if is possible to obtain more correct value of DS.

6.3 Final Appreciation

I think it was a good experience to perform the project in a different country because now I'm more prepared to different kind of situations.

In the aspect of the project it was very interesting to perform the project in an area that I didn´t feel very comfortable, but becoming very interesting after my involvement in this.

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Appendix A - Synthesis of Ethylketene Dimer

The Ethylketene Dimer was prepared from n-Butyryl Chloride represented in Figure bellow.

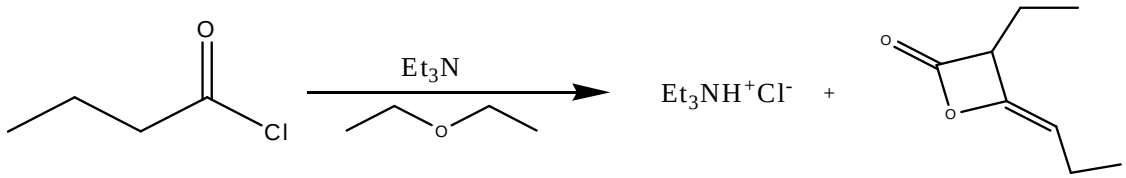

Figure A1: *Synthesis of Ethylketene Dimer with n-Butyryl Chloride.*

Into a three-necked round – bottomed flask equipped with a reflux condenser carrying a Calcium Chloride tube of an Anhydrous Ether (600 ml) and starts stirring with n-Butyryl Chloride (113 g, 1,06 mmol). After that was added slowly Triethylamine (100 g, 1 mol) and the mixture was stirring during 90 minutes. Than the mixture was cooled to room-temperature and let it stand overnight [12, 13]. The reaction of the mixture is exothermic.

The solution is removed by filtration method and was done evaporation to remove must of the Ether in the solution. After that the distillation bulp-to-bulp to remove completely the solvent and purify must part of the reagent.

In the ***Figure A2*** is represented the IR spectra of the product obtain after this experience where is possible to see that the reaction was made correctly comparing with the spectra of Diketene [19].

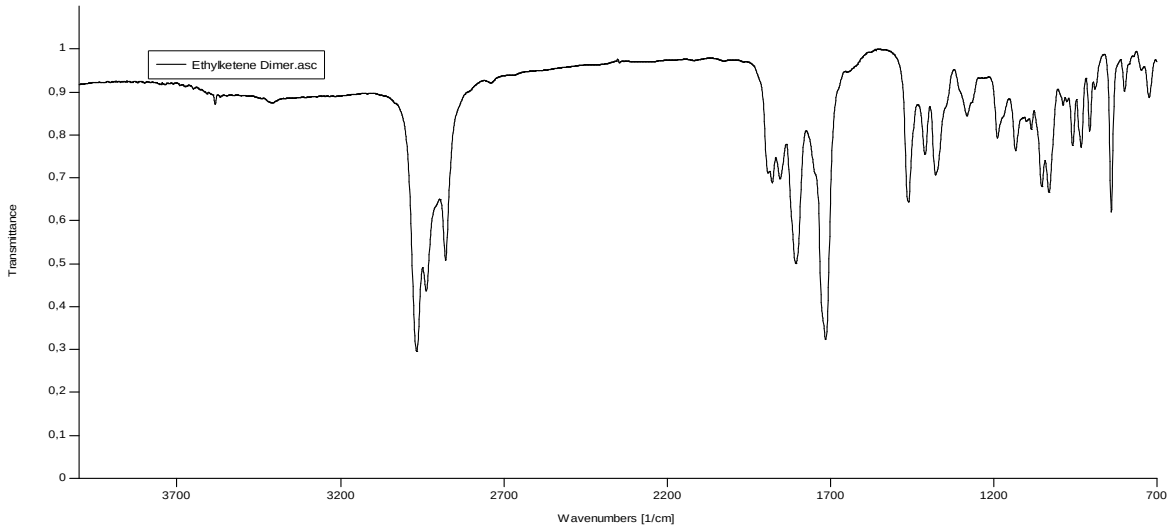

Figure A2: *IR spectra of Ethylketene Dimer.*